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Characterisation of five coins from the archaeological heritage of Portugal

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Abstract This paper reports a study carried out on three
Roman and two Portuguese coins found in the archaeological
site of São Pedro, in Fronteira (Alentejo, Portugal). The
three Roman coins have been identified as a Follis, an
AE 2 and an AE 3 (bronze alloys), while the Portuguese
coins have been identified as a Ceitil (copper) and the "6
vinténs" (Ag–Cu alloy). Scanning electron microscopy
(SEM) coupled to energy dispersive spectroscopy (EDS)
has allowed the semi-quantitative determination of the
elemental composition of both the corrosion products and
the alloy used in the manufacture of the coins. The
crystalline corrosion products constituents of the patinas
were identified by X-ray powder diffraction spectroscopy
(XRD). The more deteriorated coin, the AE 3, was submitted
to electrochemical studies in Na_2SO_4 aqueous solution and
the corresponding data analysed. After 3 weeks, the E_{OCP}
was still quite stable, ranging between −0.050 and −0.070 V
vs. SCE; the corrosion resistance, R_p, was of the order of 5 to
3×10^3 Ω. Chemical treatment of the sample by 1-h
immersion in 0.1 M NaOH produced a more active surface,
with R_p showing a decrease of a factor of about ten. On the
other hand, it was concluded from voltammetric data that
polarisations of $E_a \geq 0.050$ V vs. SCE led to copper
oxidation, with no reduction of the other corrosion products.

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Introduction

Studies of archaeological artefacts can improve knowledge
in the field of long-term corrosion providing help to
scientists and conservators to control and stop the process
of deterioration of ancient and historic metals in museums,
or in selecting ideal storage conditions.

Ingo et al. [1, 2] analysed two bronze Roman coins and
artefacts and they identified uncommon corrosion com-
pounds such as a lead chlorine-phosphate complex (pyro-
morphite, $Pb_5(PO_4)_3Cl$) and a gold-like thick layer of an
iron and copper sulphide (chalcopyrite, $CuFeS_2$). They
attributed the formation of those products to the interaction
with the soil enriched in phosphorus by the accidental
presence of a large amount of bones or to an anaerobic and
humus rich soil.

Serghini-Idrissi et al. [3] performed an electrochemical and spectroscopic study on the characterisation of patinas formed on one archaeological bronze coin from the Morocco heritage. They analysed the in-depth structure and the composition of both patina and substrate alloy by SEM observations, EDS and Raman spectroscopy.

In a recent paper, Rémazeilles and Conforto [4] presented a study on a buried Roman bronze inkwell covered with uncommon corrosion products, which they related to the interactions of the metallic piece with the agricultural fertilisers used for a long time in the soil where the archaeological site was located.

We have published a previous study [5] on another AE 3 exemplar dated from the 337–340 A.D. which was also in a quite deteriorated state.

This paper deals with the characterisation of three Roman and two Portuguese coins from a 50-coin collection found in the archaeological site of São Pedro, in Fronteira (Alentejo, Portugal), during excavations that occurred in the period 2001–2005 [6]. The Roman coins are an AE 2, an AE 3 and a Follis and the Portuguese a Ceitil and a "6 vinténs"[1].

During the Roman Republic and Empire the coins circulating in the Iberian Peninsula (Spain and Portugal) were mainly made of bronze, some of them plated with a very thin layer of silver. Until 361 A.D., these coins easily circulated in the Iberian Peninsula. However, since the emperor *Claudius* (41–54 A.D.) decided to close all the Iberian mints and transferred all the production to Rome, the monetary circulation started to decrease. After the fifth century, the circulation of Roman coins in the Iberian Peninsula, and therefore in Portugal, was significantly reduced. The three Roman coins were made of bronze alloys.

The set of Portuguese coins found in the archaeological site consisted of coins dated from the fourteenth until the nineteenth century. In this study, one coin dated from the XVI (1521–1551) identified as a Ceitil of D. João III made of copper and another one from the eighteenth century (1706–1750) identified as one "6 vinténs" of D. João V, made of Ag–Cu alloy, were analysed.

Since a wide variety of alteration products have been found in bronze artefacts depending on the burial conditions and composition of the environment [1–5, 7–13],

we decided to present this study dealing with the identification and characterisation of the coins, including the patinas composition and its relation with the soil characteristics. Optical microscopy (OM), energy dispersive spectroscopy (EDS) and X-ray powder diffraction spectroscopy (XRD) were the main techniques used for the characterisation of the surface morphology, elemental composition and crystalline corrosion products, respectively. Due to restrictions imposed by archaeologists, the exemplars should be maintained intact; without the removal of, at least, a fraction of the corrosion products, the inner layer and the substrate composition could not be determined. Nevertheless, it was allowed to remove a fraction of the corrosion products from one single exemplar that was in a quite deteriorated state; EDS spectra were obtained.

As reported by Doménech-Carbó [14, 15], Costa et al. [16], Barrio et al. [17], Serghini-Idrissi et al. [3], Scholz et al. [18], among others, electrochemical techniques, namely voltammetric techniques, are valuable tools that can provide significant analytical data useful in the fields of conservation and restoration of cultural artefacts. Costa et al. [16] emphasised the advantages of linear sweep voltammetry (LSV) as an alternative analytical tool, which combines accessibility (i.e. low cost and portability) and high sensitivity.

The present paper comprises an electrochemical study performed on the AE 3, one exemplar that was in a quite deteriorated state. The coin was immersed in an inert electrolyte, a neutral 0.1 M Na_2SO_4 aqueous solution, and the stability or alteration of the state of its surface was followed by open circuit potential measurements, E_{OCP}, continuously performed during a period of 3 weeks. Polarisation curves were also recorded and analysed leading to the corrosion parameters, R_p, I_{corr} and E_b.

Modifications induced by chemical treatments, such as immersions in 0.1 M NaOH aqueous solution, were evaluated from CVs recorded at 0.1 V s^{-1} and the corrosion parameters were obtained from the analysis of the polarisation curves recorded at 0.1 mV s^{-1}.

This study demonstrates the applicability of cyclic voltammetry as fingerprint of the state of the coin surface before and after the chemical treatment. LSV allows the determination of the suitable potential to perform the anodic stripping (dissolution) of the corrosion products.

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[1] "AE"—copper-alloy coins minted in the late Roman Empire; "AE 2": 22–27 mm; "AE 3": 17–21 mm. "Follis"-large silvered bronze coin introduced in about 294 with the coinage reform of Diocletian. "Ceitil"—copper coin of Portugal, first issued by João I (1385-1433); the coin's name is supposed to be derived from Ceuta (city in North Africa) although they were struck in Lisbon and Oporto, as well as in Ceuta. "6 vinténs"—silver coin from Portugal, with a value of 120 réis, first issued in eighteenth century.

Experimental

Archaeological site and sampling

The archaeological site consists of an extensive Roman *villa* (ca 3 ha) partially reoccupied by a mediaeval church.

The archaeological works have been focused in two places, one in the area of the stores denominated São Pedro unit (SPD) and the other under the mediaeval church of São Pedro, denominated as ISP unit. It is believed that the SPD unit was part of the *pars rustic villa* used for the storage of agricultural and other products. All the Roman coins were found in the SPD unit (stores of the Roman *villa*), and the Portuguese in the ISP unit (under the ruins of the mediaeval church of São Pedro).

The soil characteristics

The archaeological site of São Pedro is located deep in the countryside. The climate is quite dry with average temperatures ranging from ca 7 to 40 °C. The hydrogeological context of the archaeological site is a quite particular one. There is an intrusive contact between the mafic and ultramafic rocks associated with the main regional NNE-SSW trending fault of the Iberian Peninsula and sulphur thermal ground waters used as thermal waters since the Roman occupation. Most commonly, the soil contains only serpentine minerals (lizardite, antigorite and chrysotile), magnetite and residual chromite, plus brucite and carbonates [19].

The site of São Pedro may have been used for agriculture after the middle of the eighteenth century. Being an agricultural area the soil was certainly subject to the application of fertilisers (organics, humus and mineral products) and ploughed upside down, allowing the access to water and air.

Soil samples collected from both units (SPD and ISP) during excavations were analysed using standards methods [20–22]. The soil resistivity was measured with an impedance metre from Electro and Scientific Industries, Portland, Oregon, USA. A portable pH metre, Meterlab® PHM 201, from Radiometer analytical, was employed for pH measurements. A Fluke Digital Meter 8600A was used for the potential measurements. The redox potential was measured with a platinum electrode using an Ag|AgCl|3 M KCl electrode, from Metrohm, as the reference. A salt bridge connected the Pt electrode (indicator) dipped in the soil and the reference electrode compartment. Equilibrium has been allowed to be reached for 1 h.

Electrochemical studies

Electrochemical measurements were obtained *via* an AUTOLAB® PGSTAT12/General Purpose Electrochemical System (GPES) from Eco Chemie B.V. (The Netherlands). All experiments were conducted keeping the electrochemical cell inside a Faraday cage. A classical three-electrode cell was used. The reference and counter electrodes were a saturated calomel electrode (SCE) and a platinum grid, respectively.

The coin (i.e. working electrode) was soldered to a copper wire, which was insulated from solution with epoxy resin. The inert electrolytic solution used in this study was 0.1 M Na_2SO_4.

The open circuit potential, E_{OCP} between the working (coin) and the reference electrodes was measured for 2 weeks, keeping the counter electrode disconnected. This was then connected and the electrochemical polarisation applied. Disconnecting again the counter, the E_{OCP} was measured during the following week. Linear and cyclic polarisations were then re-applied and the corresponding curves recorded and analysed using the GPES software, the linear regression and the Tafel plots analysis. Then, the coin was chemically treated, by 1-h immersion in 0.1 M NaOH, washed and placed in the cell containing 0.1 M Na_2SO_4. After a rest period of ca 30 min for stabilisation of the E_{OCP}, the potentiodynamic polarisation was applied and the corresponding curves recorded.

SEM/EDS and XRD studies

A stereomicroscope was used to image the obverse and the reverse of the coins under analysis. Samples were visualised without any surface preparation in order to keep them intact. SEM studies were performed using a scanning electron microscope (JEOL, model JSM-6400). The EDS spectra were recorded with an INCA X-ray microanalysis system (Oxford Instruments).

An energy dispersive X-ray detector (model Inca X-sight, Oxford Instruments) was employed. X-ray powder diffractograms were obtained with a Philips PW 1710 diffractometer equipped with a graphite monochromator coupled with a vertical goniometer (PW 1820). The X-ray source (Cu-Kα radiation) was operated at 30 mA and 40 kV, with automatic data acquisition (APD Philips, v 3.6 B, software). Diffractograms were obtained in the 2θ ranges of 3 to 90º, at a scan rate of 0.02º s^{-1}.

Results and discussion

Soil analysis

Table 1 provides some physical properties and chemical composition of the two soil samples: one from the ISP archaeological unit (under the church ruins) and the other one from the SPD unit (under the stores of the Roman *villa*). They are neutral soils, with high resistivity, containing high amounts of P, N, Fe and K. However, the percentages are higher on the ISP unit. The organic matter is quite high, ca 10%, in the ISP unit and only ca 0.7% in the SPD unit. The high percentages of P and organic matter are probably related to the amount of bones

Table 1 Characteristics of the soil from the archaeological site of São Pedro in Fronteira (Portugal)

Soil sample	ρ (kΩ cm)	pH	E_{redox} V vs. SCE	%	[Fe] (m kg^{-1})	[Cu]	[P]	[K]	[Pb]	[N]	[N]	[Cl]
ISP (church)	9	7	+0.326	9.4	44600	87	2400	4300	7	1256	1.5	7.6
SPD (stores)	14	7	+0.280	0.7	52300	47	1800	2800	119	556	2.7	4.4

also found during the excavations. Being an agricultural area the fertilisers may also contribute to the high values of N and K. The presence of Pb in the soil corresponding to the SPD unit (119 mg kg^{-1} against 7 in the ISP unit) may be related with the hunting materials and/or the arms, munitions or explosives used by the French–Spanish troops. In the sixteenth century, they destroyed the Castle of Cabeço de Vide, located 500 m from the archaeological site.

The redox potentials of the soils samples are +0.326 and +0.280 V vs. SCE, for the ISP and SPD soil samples, respectively. These values are within the limits between a non-aerated and an aerated soil, consequently with a moderate tendency to oxidise [20–22]. Considering the values of the parameters, ρ, pH and E_{redox}, the soils can be classified as moderately aggressive soils.

The coins: visual observations and historical data

Visual observations and historical data of the five coins object of this study are given in Table 2. As can be observed on photographs presented in Fig. 1, the Roman coins exhibit quite heterogeneous surfaces covered with mineralized corrosion products giving coloured patinas, green on the Follis and the AE 2 and a yellowish coloured and quite powdered patina on the AE 3. Regarding the two Portuguese coins, the Ceitil of D. João III presents deterioration particularly visible on the borders, while the "6 vinténs" of D. João V shows a uniform and very well-preserved surface. On the left side of Fig. 1e, the obverse of the "6 vinténs", the Portuguese Royal Crown is represented, while on the right side the reverse of the "6 vinténs" shows the Cross that is the symbol of the Portuguese Military Christ Order. The symbols are easily readable on both

coins, particularly on the "6 vinténs" (see photos of details in Fig. 1f).

The colours of the surface layers vary from light to dark green, yellowish to brown over reddish layers and on the "6 vinténs" from white to grey. We believe that as reported by Robbiola et al. [7] on buried objects, the colour is strongly influenced by the soil composition.

EDS data

Table 3 gives the approximate elemental composition of the corrosion products (outer layer) of three Roman and two Portuguese coins. The spectra were acquired on zones with distinct colours.

The EDS data reveal average compositions of the products on the Follis surface differing mainly in the percentages of Ag and Si. For the AE 2, there are zones differing mainly in the percentages of Cu and Pb, i.e. zone y (26%Cu+15%Pb), while other zones present values of 11% Cu+26% Pb. The light green and the reddish brown coloured zones of the AE 3 differ mainly in the percentage of O, Si and Cu.

In the case of Ceitil of D. João III, C (33–43%), O (28–29%) and Cu (20–32%) mainly compose the corrosion layer. On the other hand, the "6 vinténs" presents non-attacked surface covered by a very thin layer composed by O (30–42%) and Cu (6–8%), apart from Ag (22–47%). Si and Cl were also detected in percentages ranging between 4% and 6%, while calcium, phosphorus, aluminium and probably even iron are present in minor amounts (<3%). All those elements are certainly exogenous elements originated from contamination by the soil during the patina formation or even dust from the soil incrusting the corrosion products. The same is valid for oxygen and carbon.

Table 2 Historical data, weight (m), diameter (Φ) and patina colours

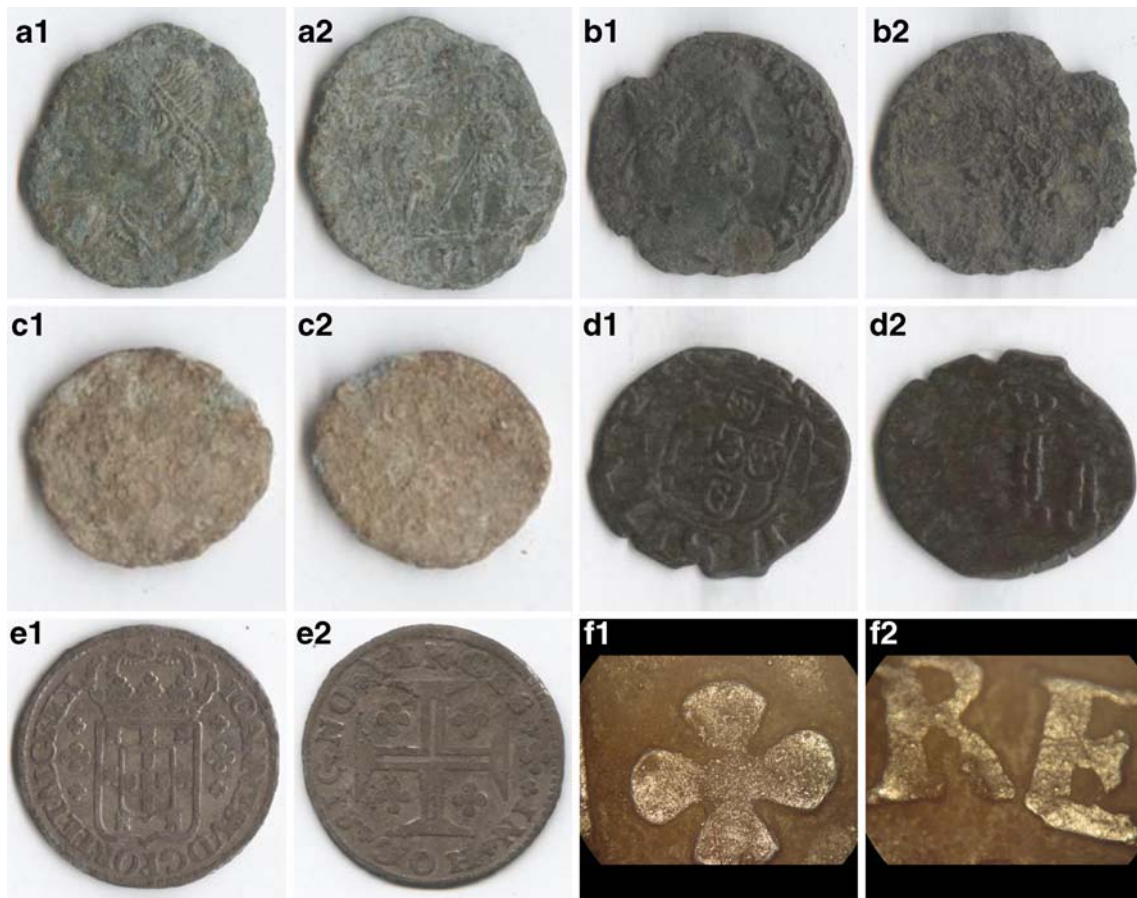| Sample Nº	Archaeological unit	Name	Imperator /kingdom	Date	m (g)	Φ (mm)	Patine
3	SPD 2-01 UE22	Follis	Constantius II	347–348 A.D.	3.36	20	Green -yellowish
4	SPD 2-01 UE44	AE 2	Maximus	383–387 A.D.	3.22	21	Dark green
6	SPD 6-05 UE70	AE 3	?	Roman period	0.91	12	Yellowish
11	ISP 1-01 UE1	Ceitil	D. João III	1521–1551	1.16	15	Dark green
13	ISP 6-05 UE30	"6 vinténs"	D. João V	1706–1750	3.35	23	White–grey

Fig. 1 Photographs of the obverse and reverse sides of the **a** Follis; **b** AE 2; **c** AE 3; **d** Ceitil; **e** "6 Vinténs"; **f** details on the surface of the "6 Vinténs"

An examination of the cross-section would help in the determination of the exact composition of the substrate, but conservators hesitate to remove the corrosion layer or damage the original piece.

On the AE 3, which was quite deteriorated in some zones, corrosion products were slightly removed therefore it was possible to acquire the spectra of the inner layer and the substrate. The analysis of such spectra is given in Table 4.

Comparing the Cu content in both the substrate and the corrosion products, we may conclude that the amount of copper salts in the latter is quite low relatively to the percentage of copper present in the substrate. On the other hand, the alloy (substrate) does not contain Fe, while percentages of 3% were found in the outer layer. The exact composition of the substrate is 69% Cu+30% Pb+1% Sn, a leaded bronze with a small percentage of Sn. As expected, the contents of O, C, Fe, Ca and Si decrease significantly from the outer to the inner layer.

XRD data

The X-ray diffraction patterns of the patinas of the five coins are given in Fig. 2. Table 5 summarises the main

Table 3 Semi-quantitative elemental composition of the corrosion products (data in % w/w)

Coin	Zone	C	O	Si	Fe	Cu	Sn	Pb	Ag
Follis	x	30	26	8	1	9	3	18	1
	y	27	26	3	1	9	2	21	8
Vestiges of Mg, Al, P, Cl, K, Ca and As (≤4%)									
AE 2	x	28	22	3	4	11	2	26	–
	y	20	19	3	10	26	3	15	–
Vestiges of Al, P, Cl and Ca (≤4%)									
AE 3	x	7	27	2	–	17	6	34	1
	y	9	37	8	5	5	–	30	–
Vestiges of Mg, Al, P, Cl and Ca (≤6%)									
Ceitil	x	33	28	3	–	32	–	–	–
	y	43	29	3	1	20	–	–	–
Vestiges of Mg, Al, Cl, K and Ca (≤4%)									
"6 vinténs"	x	7	30	5	1	6	–	–	47
	y	12	42	9	3	8	–	–	22
Vestiges of Mg, Al, Cl, K and Ca (≤4%)									

Table 4 Analysis of the EDS spectra of the outer and inner layers and of the substrate of the AE 3

% (w/w)	C	O	Mg	Al	Si	P	Cl	Ca	Fe	Cu	Sn	Pb	Ag
outer layer	7	30	1	1	5	4	1	1	3	11	3	32	1
inner layer	3	6	–	0	–	–	3	–	1	60	1	26	–
Substrate	–	–	–	–	–	–	–	–	–	69	1	30	–

crystalline compounds identified on the X-ray diffractograms. According to data in Table 5, the most probable crystalline compounds are $Pb_5(PO_4)_3Cl$ on the Follis, $Pb_5(PO_4)_3Cl$, $Pb_8Al_2Si_4O_{19}$ and $Pb_8Cu(Si_2O_7)_3$ on the AE 2, $Pb_5(PO_4)_3Cl$ on the AE 3, Cu_2O on the Ceitil and SiO_2 plus AgCl on the "6 vinténs". The dark green colour observed on the Ceitil and on other coins made of alloys containing copper may be due to amorphous copper carbonates and/or copper acetates which were not analysed. The light green colour observed on the patina of the Roman coins is probably related with the presence of pyromorphite, while the white to grey colour on the "6-vinténs" is most probably due to the presence of silver chloride and silicon oxide. The yellowish colour on the AE 3 is likely related with the presence of lead and tin oxide.
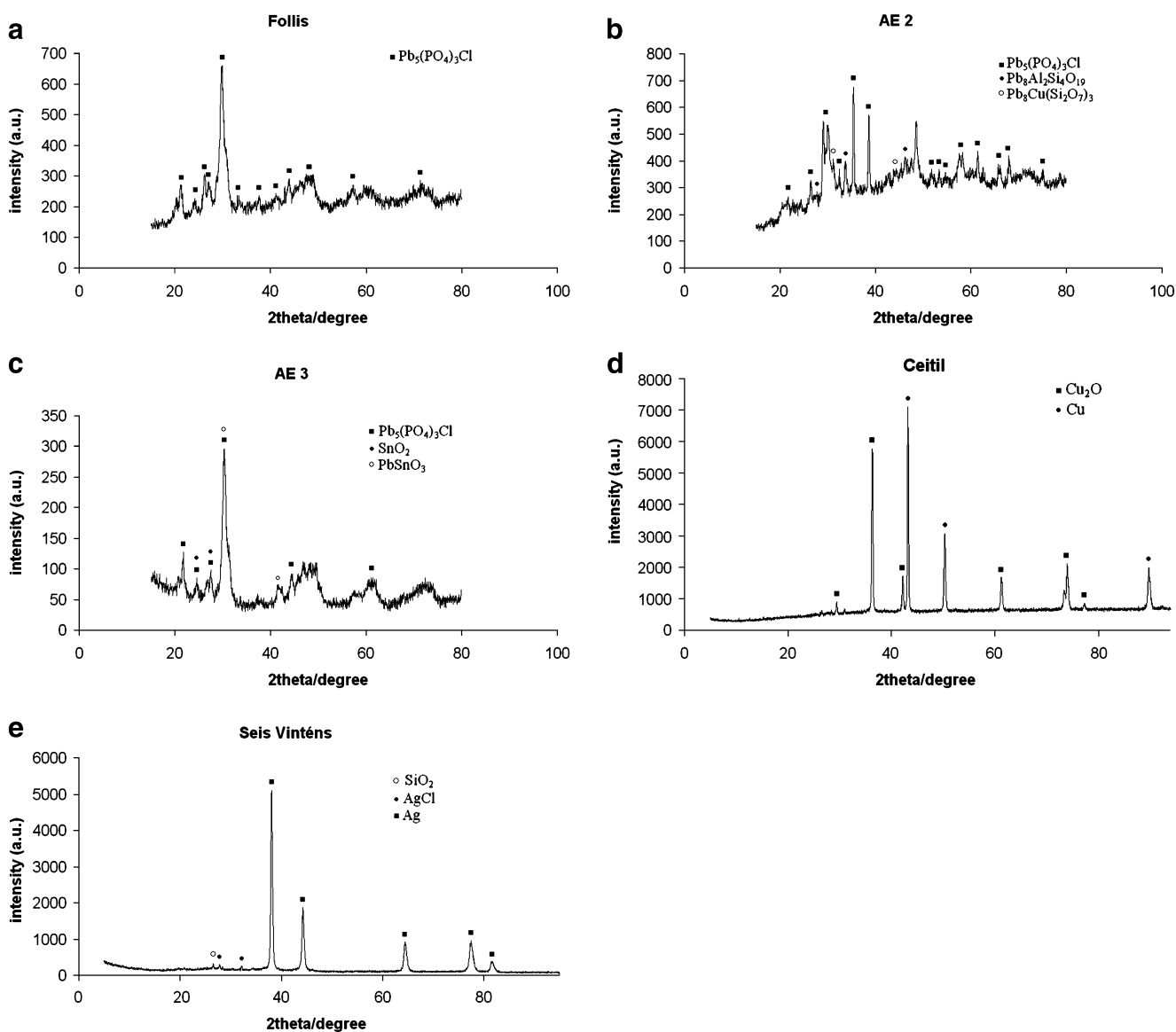

Fig. 2 XRD spectra of the corrosion products on the five coins: **a** Follis; **b** AE 2; **c** AE 3; **d** Ceitil; **e** "6 Vinténs"

Table 5 Crystalline corrosion products identified by XRD data

Coins	Crystalline compounds	Designation
Follis	$Pb_5(PO_4)_3Cl$	Lead phosphate chloride (pyromorphite)
AE 2	$Pb_5(PO_4)_3Cl$	Lead phosphate chloride (pyromorphite)
	$Pb_8Al_2Si_4O_{19}$	Lead aluminium silicates
	$Pb_8Cu(Si_2O_7)_3$	Lead copper silicates
AE 3	$Pb_5(PO_4)_3Cl$	Lead phosphate chloride (pyromorphite)
	SnO_2	Tin oxide
	$PbSnO_3$	Lead tin oxide
Ceitil	Cu_2O	Cuprite
"6 vinténs"	$AgCl$	Silver chloride (chlorargyrite)
	SiO_2	Silicon oxide

In many other studies of buried archaeological objects made of copper alloys, the patinas have been found to be composed by copper, lead and tin oxides, carbonates, silicates and phosphates. Ling et al. [8] identified on corroded bronzes Ding from the Yin Ruins of China compounds such as: $Cu_2(OH)_3Cl$, $Cu_2(OH)_2CO_3$, $Cu_3(CO_3)_2(OH)_2$, CuO, $CuCO_3$, $PbCO_3$, Pb_3O_4, PbO and SiO_2. Also, Ingo et al. [9] found uncommon compounds among the corrosion products of bronze coins, such as a lead chloride and phosphate complex, $Pb_5(PO_4)_3Cl$, and a thick layer of an iron and copper sulphide, chalcopyrite, $CuFeS_2$. Scott and Fabrizi [10, 11] also found unusual copper corrosion products on buried copper artefacts. A Raman band attributed to a mixed copper–lead oxychloride, $Cu_{20}Pb_{21}Cl_{42}(OH)_{40}$ (cumengéite) was identified by Frost et al. [12, 13].

In a recent paper, Rémazeilles and Conforto [4] have reported $Pb_5(PO_4)_3Cl$ on the patinas of a buried bronze coin.

Electrochemical studies

The open circuit potential, E_{OCP}, of the AE 3 (Cu–Pb–Sn alloy) immersed in an inert electrolyte (i.e. 0.1 M Na_2SO_4) was followed during 2 weeks. The recorded values were quite stable ranging between −0.05 and −0.08 V vs. SCE. Acting as the working electrode, the coin was submitted to linear and cyclic potentiodynamic polarisations, between −0.500 and +0.050, at 0.1 V s^{-1}. After this set of electrochemical tests, the working electrode was again left at open circuit potential during one week. The electrochemical experiments were then repeated. After 1-h immersion in 0.1 M NaOH, the coin was washed with distilled water and re-introduced in the electrochemical cell containing 0.1 M Na_2SO_4. After ca 30 min, the electrode was polarised under experimental conditions identical to those of the previous experiments. Figure 3 presents a set of linear polarisations curves of the coin in 0.1 M Na_2SO_4, after different immersion periods (14 and 21 days) and after dipping it in 0.1 M NaOH for 1 h.

Another set of linear polarisations curves was recorded in a more limited potential range, at very slow scan rate, i.e. at 0.1 mV s^{-1}. These curves were analysed using the linear regression method and the Tafel plots analysis. The obtained parameters are given in Table 6.

Cyclic voltammograms were recorded at 0.1 V s^{-1}, between various anodic limits of potential (from −0.500 to +0.080 V); Fig. 4 illustrates the obtained set of results. The cathodic peak at ca −0.030 V is due to the electrochemical reduction of Cu^{2+}. Its size increases as the anodic potential is extended to the anodic direction. After running this set of cyclic voltammograms, the surface of the coin was observed and the reddish colour characteristic of the active Cu could be visualised; however, residues of the mineralized or incrustated corrosion products were still remaining.
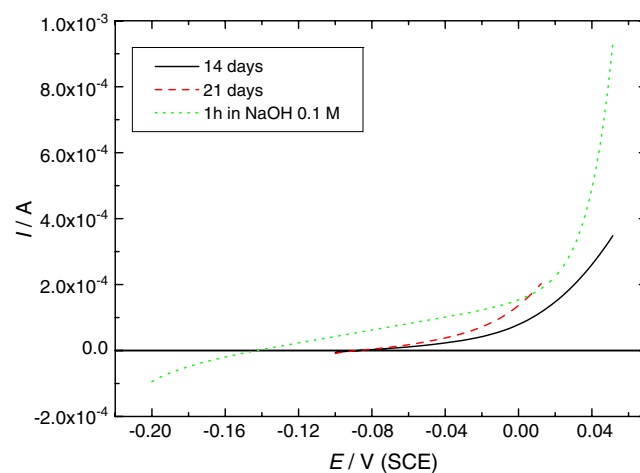

Fig. 3 Linear polarisation curves of the AE 3 in 0.1 M Na_2SO_4 after: (*black solid line*) 14 days; (*red broken line*) 21 days; (*green broken line*) 1 h in 0.1 M NaOH. $\nu = 1$ mV s^{-1}

Table 6 Kinetic corrosion parameters from the linear regression and Tafel slope analyses of the polarisation curves recorded at $\nu=0.1$ mV s^{-1}

Immersion conditions	R_p (Ω)	E_{corr} (V vs. SCE)	E_b	R_p (at $E=E_{corr}$) (Ω)	I_{corr} (μA)
14 days in 0.1 M Na$_2$SO$_4$	5.4×10^3	−0.106	−0.010	5.6×10^3	1.6
21 days in 0.1 M Na$_2$SO$_4$	3.1×10^3	−0.079	−0.020	3.3×10^3	3.1
22 days in 0.1 M Na$_2$SO$_4$+1 h in 0.1 M NaOH	0.9×10^3	−0.143	−0.040	0.9×10^3	13.0

From the electrochemical studies, it was concluded that anodic polarisations in neutral medium consisting of Na$_2$SO$_4$, at potentials lower than 0 V vs. SCE, would not introduce alterations on the coin surface. However, higher anodic potentials such as $E_a \geq +0.050$ V may lead to the dissolution of copper without removing the undesirable residues from the corrosion products present on the coin surface. Nevertheless, 1-h immersion in 0.1 M NaOH led to a surface less resistant to corrosion. Electrochemical studies on the AE 3 exemplar will pursue.

Conclusions

The here-studied three Roman coins were found under the ruins of the stores of the Roman *villa* (SPD unit), while the Portuguese coins were from the ISP unit, under the ruins of the mediaeval church. Both soil samples are rich in P, N, K and Fe. However, the soil from the ISP unit presents higher values for those elements and for the organic matter (10% against 0.7%).

The EDS data have identified Cu and Pb on the Roman coins, Cu on the Ceitil and Ag plus small percentage of Cu on the "6 vinténs". The exact composition of the AE 3 is 69%Cu+30%Pb+1%Sn; the other two Roman coins were also made of leaded bronze alloys. Regarding the Portuguese coins, the Ceitil is made of copper and the "6 vinténs" is made of silver with a small percentage of Cu.

The crystalline corrosion products identified by XRD as constituents of the patinas (outer layers) of the Roman coins were a lead phosphate chloride complex, Pb$_5$(PO$_4$)$_3$Cl, on the Follis, the same lead phosphate chloride complex, Pb$_5$(PO$_4$)$_3$Cl, plus lead and aluminium silicate, Pb$_8$Al$_2$Si$_4$O$_{19}$, and lead and copper silicate, Pb$_8$Cu(Si$_2$O$_7$)$_3$, on the AE 2 and again the lead phosphate chloride complex, Pb$_5$(PO$_4$)$_3$Cl, plus tin oxide and lead and tin trioxide on the AE 3. On the Portuguese coins, only cuprite, Cu$_2$O, was identified on the copper-made Ceitil, and on the "6 vinténs", the coin containing high percentage of Ag, AgCl and SiO$_2$.

The electrochemical study on the AE 3 (Cu–Pb–Sn alloy) demonstrated that, after a 3-week immersion in a neutral Na$_2$SO$_4$ solution, the state of the coin surface was quite stable. Polarisation potentials higher than 0 V led to copper oxidation.

Electrochemical data have also shown that the chemical treatment with NaOH aqueous solution leads to a less resistant surface, with copper dissolution occurring before the electrochemical reduction of the other alteration products or residues present on the coin surface.

Electrochemical studies with the AE 3 will pursue.

Fig. 4 Cyclic voltammograms of the AE 3 after 14 days in 0.1 M Na$_2$SO$_4$, at various anodic limits of the polarisation potential, E_a. E_i=−0.500 V *vs.* SCE. $\nu=0.1$ V s^{-1}

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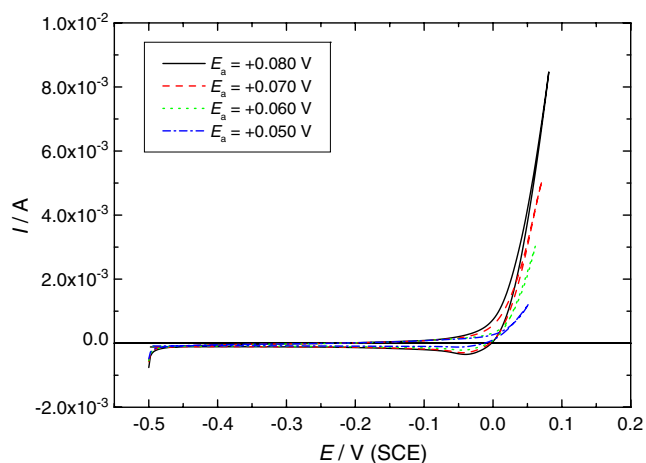
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